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# In-depth comparison of morphology, microstructure, and pathway of char derived from sewage sludge and relevant model compounds

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2	derived from sewage sludge and relevant model compounds				
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#### 21 Abstract

Hydrothermal conversion (HTC) of sewage sludge (SS) and its relevant model 22 23 compounds such as cellulose, glucose, lignin and soybean protein (substitute for protein) was experimentally conducted at moderate reaction temperature of 260 °C for 24 60 min. The structural properties, carbon-containing groups, and microstructure of the 25 char were characterised by several techniques. The results revealed that more benzene 26 rings were formed by small clusters and the C-O bond on Aryl-alkyl ether 27 decomposed on the surface particles during the HTC process. In addition, the catalyst 28 29 Zeolite Socony Mobil–5 (ZSM-5, Si/Al: 300) showed an excellent performance on the high graphite degree of the char under moderate reaction temperature of 260 °C. In 30 particular, cellulose has the most dramatic influence on the depolymerisation of 31 32 C-(C,H). As evidenced with SEM, the size of the char derived from SS with ZSM-5 catalyst is 10-15µm, which is smaller than the char without catalyst. A mechanism for 33 derivation of char from individual model compounds is proposed. The end products of 34 35 lignin are composed of polyaromatic char, while the composition of the char derived 36 from protein suggests that polymerisation may occur during hydrothermal reaction leading to formation of structures with N-containing compounds. 37

38 **1. Introduction** 

Sewage sludge (SS) is a combination of post-treatment water-carried residues produced in a wastewater treatment plant and is by far the largest waste component of the plant. Besides the high volume, sewage sludge may contain certain contaminants, including heavy metals, hazardous organic and inorganic substances, as well as

pathogenic microorganisms (He et al., 2013; Zhai et al., 2016), which can threaten the 43 environment if not disposed properly. To date, the thermochemical route has been 44 45 regarded as an effective way to convert the biomass into bioenergy (Ahmad et al., 2018; Zhang et al., 2018), wherein the organic matter in the SS can be reused to 46 generate energy or high value products. However, the process should also enhance the 47 reduction of the toxic substances, the stability of heavy metals and the dehydration of 48 the SS as well, so that the end products could be reused with less environmental 49 consequences. For these reasons, hydrothermal conversion (HTC) of SS has emerged 50 51 as a promising approach to convert the SS into value-added products (Stirling et al., 2018). The process involves heating the SS at 180-300 °C, and at an autogenic 52 pressure of 2-10 MPa for a short duration in an inert atmosphere (Areeprasert et al., 53 54 2014; Chen et al., 2015). Previous researches have proved that various biomass wastes can be treated by using HTC, especially those with high moisture content, 55 including algae, sewage sludge and digestate (He et al., 2014; Mumme et al., 2015; 56 Peng et al., 2016; Thiruvenkadam et al., 2015). Patel et al. (Patel and Hellgardt, 2015) 57 investigated a novel continuous hydrothermal liquefaction reaction in microalgae 58 which conducted at 300-380 °C for a quick reaction of 0.5-4min. The highest 59 biocrude yield was 38 % and was obtained at 380 °C. Furthermore, it is possible to 60 produce high-quality biocrude by reducing the oxygen and nitrogen content in the 61 microalgae during the process. He et al. (He et al., 2013) applied HTC to SS to gain 62 63 fuels. They examined the hydrothermal carbonisation of SS at 200 °C for 4-12 h. Their experimental results demonstrated that most of the carbon can be recovered and 64

65	HTC also has the ability to remove nitrogen and sulphur. Compared with SS,
66	hydrochar shows a better performance on stabilisation with a high heating value
67	(HHV). Similar results were also found by a previous study (Lu et al., 2011), that
68	conducted a comparative research on the HTC of three types of municipal solid waste
69	from Japan, China, and India, respectively. The researchers observed that the HTC
70	process caused an approximately 6.4-9.0 fold enhancement in the heating value (HV)
71	of MSW. Furthermore, HTC appears to be a clean technique that can remove the
72	nitrogen content from SS as a pretreatment process (Shen et al., 2018). Therefore,
73	HTC can be considered an environmentally friendly method with a bright potential.
74	In addition, a range of catalysts also play a crucial role during the treatment, which
75	significantly impacts the HTC process. To achieve different corresponding end
76	products, various catalysts, including CaO, CH2O and Zeolite Socony Mobil-5
77	(ZSM-5) have been used during the treatment (Du et al., 2013; He et al., 2015; Kang
78	et al., 2012b). Previously, He et al. (He et al., 2015) carbonised SS with CaO to
79	produce gaseous, solid, and liquid products for energy recovery. They indicated that in
80	high reaction temperatures, CaO as a chemical additive had a positive effect on H <sub>2</sub>
81	yield and the hydrolysis process. In another study (Kang et al., 2012b), formaldehyde
82	as a polymerization agent has been applied in the HTC of black liquor under reaction
83	temperatures ranged of 220 to 285 °C, indicating that the char yield, HHV, and carbon
84	recovery efficiency increased with the formaldehyde assistance. On the other hand,
85	technically produced zeolites have been widely used in thermal chemical conversion
86	as important catalysts (Mumme et al., 2015). It has been shown that zeolite is capable

87 of improving the energy and carbon recovery for char production.

Most researches have investigated the feasibility of the HTC process to produce 88 89 bio-products, enhance the properties of the biochar and bio-oil, and the energy balance for the conversion system (Peng et al., 2017; Toor et al., 2011; Zhai et al., 90 2017; Zhao et al., 2014). Furthermore, due to the complex composition of the SS, it is 91 reasonable to use model compounds to investigate the pathway of the char production. 92 However, studies on the morphology and microstructure of char derived from SS and 93 its model compounds by using catalytic hydrothermal conversion are uncommon. 94 95 Besides, few of them have explored the effect of ZSM-5 as a catalyst on the char products or performed a comparative study between SS and its model compounds, 96 which is crucial for studying the mechanism of the treatment (Wang et al., 2013). To 97 98 clearly understand the HTC process mechanism of SS-derived char in different condition, the first step is to investigate the characteristic of SS and its model 99 compounds-derived char, respectively. The second step is to investigate the 100 characteristic of the mixed compounds, which is composed of individual model 101 compounds. This work focus on the first step and aims to gain an insight into the 102 morphology and microstructure of the char derived from SS and its model compounds 103 by employing catalytic HTC. Individual objectives of the research were (i) to analyse 104 the morphological structure of the HTC products derived from SS and model 105 compounds; (ii) to evaluate the surface morphology of the char during the HTC 106 107 process; (iii) to comparatively describe the char properties of the SS and model compounds; (iv) to characterise and investigate the effects of ZSM-5 catalyst on the 108

HTC of SS; and (v) to discuss the probable pathway of each model compounds
through the HTC process under 260 °C. This article will help explore further in-depth
studies on the mechanisms of the char structural transformation while undergoing the
HTC process on the co-pyrolysis.

#### 113 2. Material and methods

#### 114 **2.1. Raw materials.**

As a raw feedstock, dewatered SS was provided by a wastewater treatment plant in 115 Changsha, China. Before being processed, the SS was heated in an oven at 105 °C for 116 117 24h to remove water. To homogenise raw sludge particle, they were milled and sieved into a powder, for maintaining the particle size between 0.2 and 0.25 mm. According 118 to the previous researches on its properties, SS is composed of three main organic 119 120 substances, protein, carbohydrates, and lignin (Nielfa et al., 2015; Peng et al., 2017). Therefore, protein (soybean protein), carbohydrates (cellulose and glucose) and lignin 121 were used as the model compounds in this study. Cellulose was supplied by Whatman, 122 123 glucose and soybean protein (SP) were supplied by Sinopharm Chemical Reagent Company, and lignin was obtained from Ruibio Company. Different types of ZSM-5 124 have different physicochemical properties. To comparatively study the catalyst, 125 ZSM-5 with the Si/Al ratios, 38 and 300 was obtained from Kaiwei Chemical 126 Industry company. All the raw materials were sealed in a storage bottle to avoid 127 moisture adsorption. The predominant fractions of the organic substances in the SS 128 129 were lignin (4.7%), cellulose (6.2%), glucose (7.1%), and protein (23.3%).

#### 130 **2.2. Hydrothermal carbonisation process**

The char sample was produced in a high temperature and pressure reactor, which was 131 connected to a temperature controller and an electromagnetic stirring module. Similar 132 133 to our previous study (Wang et al., 2017; Zhai et al., 2017), the reaction temperature and the holding time for each experiment were set at 260 °C and 60 min, respectively, 134 as optimization parameters. For a typical trial, 20 g SS and individual model 135 compounds were mixed with 180 g deionised water in the reactor at a stirring rate of 136 100 r/min, respectively. A mixture of SS (20 g) and ZSM-5 (10 g) in 180 g deionised 137 water was used as the control sample. For another control sample, cellulose (3 g), 138 139 glucose (3 g), SP (8 g), and lignin (6 g) and were combined vigorously in 180 g deionised water. Each experiment was initiated with an inflow of N<sub>2</sub> for 5 min to 140 remove any oxygen prior to the HTC process. After the completion of HTC, the end 141 142 products were collected and separated into solid and liquid products through filtering after cooling the reactor to room temperature. The solids were oven dried at 105 °C 143 until there was no significant change in weight and were subsequently milled into a 144 145 homogeneous powder for further analysis. Each trial was named as the feedstock followed by the synthesis specifications, namely the reaction temperature and the 146 Si/Al ratio (38 or 300). For example, the label SS-260-38 means the char was 147 produced from the SS at 260 °C with ZSM-5, that had a Si/Al ratio of 38. Moreover, 148 the mixture of the cellulose, glucose, SP and lignin was denoted as MC-260. 149

### 150 **2.3. Analysis and characterisation of char**

151 The contents of the dry matter were determined gravimetrically by heating them up at

152 105 °C for 24h. A CHNS analyzer, (2400 Series II PerkinElmer, USA) was used to

examine the elemental content of the samples. The oxygen content was calculated 153 using the difference. To determine the differences among the carbon-containing 154 groups of char produced in different trials, X-ray photoelectron spectroscopy (XPS) 155 was performed with a K-Alpha spectrometer using an Al monochromatic X-ray anode. 156 For C, the binding energy was corrected necessarily at 285.0 eV to the principal C1s 157 line. The peak fitting was carried out with Gaussian peaks. A Raman spectrometer 158 (Labram-010, JOBIN YVON, France) was employed to investigate the transformation 159 of the carbon structure. An excitation laser beam was focused by using a 160 161 charge-coupled device camera, which is equipped with a spectrometer and can record the Raman data as well. The analyser operated with a 532nm laser excitation source in 162 a range of 1000-2000 cm collected with an acquisition time of 20 s. Each spectrum 163 164 test was scanned three times to minimise the noise ratio. The morphology of the char samples were recorded using a field emission scanning electron microscopy (FE-SEM, 165

166 JEOL JSM-6700F). Before each experiment, the samples were coated with gold.

167 **3. Results and discussion** 

#### 168 **3.1. Raman analysis of char**

Gaussian and Lorentzian profiles consist of Raman bands under a typical condition for most of the disordered materials. Quantitative parameters such as intensity, full width at half-maximum and curve-integrated area can be composed by fitting the curve for the Raman spectra (Chen et al., 2019). Based on these parameters, Figure 1 shows the Raman spectra, which is decomposed by fitting eight Gaussian curves in the region from 1000 to 1800 cm<sup>-1</sup>. For the sample of SS and the char derived from

175	the model compounds, all the bands of the fitting curve in the spectra representing the
176	general structures in the char, are listed in Table 1. During the HTC process of the SS,
177	aromatic content with cross-linked structures increased significantly and small
178	polyaromatic structures decreased in the char. G and D bands represent the degree of
179	graphite, which can be considered as the most important feature in char (Sheng, 2007).
180	Moreover, as shown in Figure 2, the intensity ratio of D/G as a functional parameter
181	has a significant effect on the crystallite size or graphite-like carbon structure.
182	Compared with the SS, the D/G ratio of char, which is related to the dehydrogenation
183	of hydroaromatics, was dramatically enhanced, indicating the formation of six or
184	more benzene rings during the HTC process (Brown et al., 2017). Meanwhile, the
185	aromatic rings increased under the moderate reaction temperature (260 $^{\circ}$ C). In
186	addition, the D/G ratio value of char derived from the model compounds rose nearly
187	by the same degree, except for the SP. The D/G ratio of SP increased sharply, which
188	means there was a remarkable degree of protein decomposition in the SS. According
189	to the D/G ratios, ZSM-5 with Si/Al of 300 had a better performance on the graphite
190	degree under 260 °C reaction temperature. The D/G tendencies of glucose, cellulose,
191	and lignin were similar due to their molten state during the reaction and resulted in the
192	disorder of the char due to the formation of the aromatic carbon structure (Ferrari et
193	al., 2003). Furthermore, due to the indistinct separation between the D and G bands,
194	an intermediate band called kekule band was formed, located at wave number values
195	between 1320 and 1580 cm <sup>-1</sup> . In the case of the char derived from the SS and model
196	compounds, the kekule band comprises three bands, $G_R$ , $V_R$ , and $V_L$ , which are

197	associated with the amorphous carbon and smaller aromatic rings. Accordingly, the
198	ratio of $D/(G_R+V_R+V_L)$ represents the proportion between the large and small
199	aromatic rings in the amorphous carbon (Zhao et al., 2016). The $D/(G_R+V_R+V_L)$
200	values are shown in Figure 2. The value increases after the treatment. However, both
201	the types of ZSM-5 catalyst exert a slight reduction on the $D/(G_R+V_R+V_L)$ ratio of
202	char, indicating that more small aromatic rings in the amorphous structure were
203	formed during the reaction with ZSM-5. Notably, the $D/(G_R+V_R+V_L)$ intensity is the
204	highest in the model compounds, indicating that cellulose is the most influential part
205	in the ordering of char. Another significant transformation is in the S band, which
206	shows a huge reduction during the HTC process. This represents the corresponding
207	breakage in the C-C linkages on the hydroaromatic rings during the decarboxylation
208	reaction. With the continuing hydrothermal reaction, the C–H bonds on the arene
209	rings and C-O on Aryl-alkyl ether decomposed, resulting in formation of a
210	graphite-like carbon structure in the char (Fushimi et al., 2009).
211	3.2. XPS analysis of char
212	XPS can identify the oxidation state of the elements on the surface (2-10 nm). The
213	XPS C 1s spectra of the SS and the hydrothermal solid products obtained through the
214	HTC process are shown in Figure 3. To better identify the well-defined groups in the
215	char, curve fitting was conducted with six peaks, including several functional groups
216	such C-H groups (282.1 -283.6 eV), C-(C,H) (284.6 eV), and -C-OR groups
217	(285.7-286 eV) in hydrocarbons such as cellulose, lignin, and glucose (He et al.,

218 2016). C-(O,N) (285.6 eV) can be found in proteins and alcohols. Carbonyl or

219	quinone groups R-C=O (287.6 eV) in lipids, amides, carboxylate, acetals, and
220	hemiacetalsCOOR (288.7 -289.1 eV) groups in lactones or carboxyl (Marta and
221	Fuertes, 2009; Xia et al., 2007). To understand more details about each functional
222	group, Figure 4 compares the relative intensities of the carbon-containing group of the
223	SS, and the solid products from the SS and its relevant model compounds by using
224	Gaussian–Lorentzian fitting to calculate the relative intensity of each carbon
225	functionality. For the SS, C-(C,H) and C-(O,N) are the predominant
226	carbon-containing groups (56.39% and 30.58%, respectively), followed by minor
227	contributions from R-C=O and C-H (8.47% and 4.55%, respectively). When the
228	carbon-containing groups of the char are compared with and without the ZSM-5
229	catalyst, several functional groups show a distinct change due to the catalyst effect.
230	The intensity of C-(C,H) in sample SS-260-38 reduced sharply, whereas the C-(O,N)
231	group distinctly increased during the HTC process, indicating that the ZSM-5 (Si/Al :
232	38) favoured depolymerisation of C-(C,H) during the HTC process. In addition, the
233	transformation of the internal aromatic carbon of hydroxyl groups in linear alcohols,
234	ethers, or phenols may result in high levels of C-(O,N) group (He et al., 2016). The
235	other two peaks corresponding to -C-OR and C-H maintained relative thermal
236	stability. To obtain information on the specific transformation of carbon-containing
237	groups, the carbon functionalities of char derived from SS relative model compounds
238	were compared. The COOR, R-C=O, and C-OR groups were similar and found to be
239	dominant among glucose, cellulose, and lignin-derived char. However, the main
240	carbon-containing group in cellulose was C-(C,H) whereas no C-H groups were found,

which revealed that cellulose has a dramatic influence on the depolymerisation of 241 C-(C,H). The total intensities of COOR, R-C=O, C-(O,N), and C-OR for the char 242 243 derived from the model compounds are in the range 46.37-61.96%. This means that abundant of oxygen groups were formed from glucose, cellulose, lignin, and protein 244 on the surface of the char during the HTC process (Sevilla and Fuertes, 2009). 245 Hydroxyl, carbonyl, and ester are the reactive groups in the model compounds and 246 can easily degrade to molecular fragment and compete with the transformation of the 247 aromatic compounds. It is noteworthy that the COOR group disappeared in the 248 249 SS-derived char, which can be correlated with the influence of inorganic substances in their corresponding feedstocks. 250

### 251 **3.3. Char surface morphologies**

252 SEM was used to observe the surface morphological changes during the HTC process. Figure 5 shows the surface morphological characteristics of SS (a), SS-derived char 253 with or without catalyst (b-d), and its relevant model compounds-derived char (e-i). It 254 255 can be seen that after the HTC treatment, the char derived from SS without catalyst (b) has a size similar to the SS. However, the surface of the char is quite different 256 according to the slits. The catalytic hydrothermal char (c and d) has homogeneous 257 particles with a smaller size (10-15 µm) than the SS-derived char (25-30 µm), 258 indicating that the hydrothermal reaction was conducted thoroughly with ZSM-5 259 assistance. The char derived from the model compounds mixture (e) forms a porous 260 261 structure and several holes are apparent on the surface, which indicates a fast volatile release during the HTC process leading to the formation of several internal cavities as 262

open structures. Compared with the individual model compounds, SP-derived char (f) 263 has a relative large particle size, implying that the smaller pieces of protein particles 264 re-aggregate under 260 °C. This finding is reasonably explained by the heterocyclic-N 265 polymerization that occurs during the high temperature reaction. Due to the properties 266 of the lignin fragments, it is difficult to melt them into an aqueous phase under 267 relative low reaction temperature of less than 377 °C (Fang et al., 2008). In this study, 268 the HTC reaction temperature is 260 °C, so it results in favourable conversion from 269 solid to solid. As shown in the lignin-derived char (g), the surface is smoother than in 270 271 the other model compounds, and with no holes produced due to the emission of volatile matter. This phenomenon may be ascribed to the exposure of both dissolved 272 and non-dissolved lignin fragments to water. Afterwards, the decomposition of lignin 273 274 to phenolics due to hydrolysis and further polymerization of the phenolic char, causes its accumulation on the surface of the polyaromatic char leading to recovery of the 275 holes or cracks (Kang et al., 2012a). The cellulose-derived char (h) decomposed into a 276 277 large irregular block style structure with fewer holes and retained the fibre skeleton during the HTC process. However, compared with the earlier studies, it should have 278 formed microspheres through the hydrothermal carbonisation of cellulose (Sevilla and 279 Fuertes, 2009). The different operating parameters such as lower ratio of 280 cellulose/water and less experimental duration may have caused this difference. 281 Notably, the cellulose-derived char with aggregates of microspheres is usually formed 282 after 4 h at approximately 220 °C. Whereas in this experiment, the cellulose-derived 283 char shows the beginning of an abrupt morphological change under a higher reaction 284

temperature of 260 °C after 1 h. Similar to the glucose-derived char observation (i), it decomposed into several small particles and further formed a hydroxymethylfurfural microspherical structure. The difference in topography from the previous research can be explained by the residence time and reaction temperature. The microsphere structures are formed with an increase in the residence time and then keep growing until achieving their final size (Falco et al., 2011).

#### 291 **3.4. Individual model compounds pathway during HTC process**

292 To explore further in-depth studies on the pathway of the SS-derived char structural

transformation while undergoing the HTC process. Individual model compounds

294 pathway during HTC process should be advance considered. Combining the results

from numerous previous studies with ours on the transformation mechanism of model

compounds, including that of cellulose (Falco et al., 2011; Fang et al., 2008; Sasaki et

al., 1998; Sevilla and Fuertes, 2009), glucose (Möller et al., 2011), lignin (Pandey and

Chang, 2011; Wu et al., 2017), and protein (Su et al., 2010) through HTC, the

formation pathway of char from individual model compounds via HTC process can bereasonably schemed.

Figure S1 illustrates the main char formation pathway from cellulose and glucose under 260 °C hydrothermal reaction temperature. In the first step, cellulose chains are hydrolysed and subsequently converted into glucose and its isomerisation fructose in the range 180 to 240 °C. The time consumed in the first step decreases with the reaction temperature. The yield of glucose can reach its maximum value in the first 10 min under 200 °C (Nagamori and Funazukuri, 2010). In the subsequent reaction stage,

the monomers of the organic acids are decomposed into hydronium ions, which can 307 be considered as the catalysts for the dehydration. The monomers produced from the 308 309 hydrolysis of the oligomers undergo a dehydration reaction, resulting in the opening of the ring and breaking of the C-C bonds, and then subsequently form into various 310 furans at temperatures near 130 °C (Chheda et al., 2010; Sinag et al., 2010). Acids and 311 phenols are obtained from the decomposition of the furans with the HTC process. 312 Simultaneously, dehydration or aldol condensation and formation of aromatic 313 polymers occur as well. The hydroxyl groups in the monomers get dehydrated and 314 315 converted into C=O groups (Bacon and Tang, 1964). Aromatic clusters appear due to the condensation of the aromatic units, which are formed due to the decomposition of 316 the carbohydrates such as monosaccharides. As a result, more oxygen groups may get 317 318 concentrated on the surface of the char particles than in the core forms.

Parameters such as temperature, duration, pH, and the use of catalysts have different 319 effects on the conversion pathways and kinetics. For example, the pH of the liquid 320 321 sharply decreased at the beginning and then either remained low or slightly increased. 322 The inflection time point for the pH rise depends on the reaction temperature. Furfural and 5-HMF intermediates formation may be responsible for this trend, as they account 323 for the production of various acids, as already observed elsewhere (Reza et al., 2014). 324 Meanwhile, the pH of the liquid after the introduction of lignin to the HTC process 325 showed a tendency contrary to the result of cellulose introduction. The pH increased 326 327 with the reaction time and temperature rise, as most of the phenolic compounds are derived from lignin degradation and not from acids. According to previous tests in 328

different conditions, the content of hydrochar derived from lignin is more than that from cellulose because the structure of lignin is an aromatic molecule prone, which can be condensed with other polyphenolic compounds (Braghiroli et al., 2017; Selmi et al., 2018).

However, there is no obvious agreement on the kinetic parameters for cellulose conversion. Most open literatures show various  $E_a$  and  $K_0$  values due to the wide range of reaction temperatures, durations and catalyst use (Danon et al., 2014; Kim et al., 2011; Liu et al., 2014).

337 Lignin is a phenyl propane biopolymer, and consists of three different phenyl propane

monomer units named p-coumaryl, coniferyl, and sinapyl alcohol (Wang et al., 2018).

339 The structure of lignin can be randomly formed by the combination of those three

monomer units. Hence, the reaction pathways of lignin are complex. Figure S2

341 proposes a simplified mechanism for carbon-containing substance transformation

from lignin via the HTC process. In the first reaction stage, lignin quickly degraded

into dissolved and non-dissolved parts. When the reaction temperature was low, a part

of the lignin did not completely dissolve. The transformation of non-dissolved lignin

into phenolics required more time at a relatively low reaction temperature.

Polymerisation was then seen after prolonged residence time, which led to the

347 generation of high molecular weight polymers on the char surface. The pathway of

348 solid-solid formation from lignin is similar to pyrolysis, which produces highly

349 condensed char as well. On the other hand, a small amount of dissolved lignin was

350 exposed to water. These fragments of dissolved lignin were converted to syringols,

351	guaiacols and catechols, and were subsequently decomposed into phenols and
352	aromatics (Wahyudiono et al., 2010; Wahyudiono et al., 2009). Aromatic oligomers
353	were formed through re-polymerisation on the surface of the phenolic char in the
354	process.
355	The results of previous studies on the characteristics of the main experimental
356	parameters are similar. Typically, the bio-oil yield increases with rising reaction
357	temperatures from 250 to 350 °C (Fan et al., 2018). Furthermore, the reduction of
358	nitrogen-containing compounds can be improved by various catalysts, however, the
359	processing mechanism is not clear yet. Compared with this study, Figure S3 shows the
360	typical reaction pathway of the protein model compounds through the HTC process.
361	The amino acids were first formed by hydrolysis where the peptide bonds (C-N) from
362	the carboxyl and amine groups were broken(Peterson et al., 2008). Compared to
363	cellulose and glucose hydrolysis under natural reaction conditions, the protein
364	depolymerisation was more difficult. Due to the stability of the peptide bonds, it takes
365	a long time to complete the depolymerisation process without changing the pH value
366	or the catalyst. The Maillard reaction can be applied to generate several reactive
367	intermediates under a mild reaction temperature. At higher temperatures,
368	carbonisation and subsequent pyrolysis became more pronounced. As the
369	hydrothermal reaction temperature increased, there was a significant cyclisation of the
370	intermediates. Besides, the N-containing compounds were enhanced by
371	polymerisation which is also proved by the enhancement of the C-(O,N) functional
372	group. It is noteworthy that the hydrothermal conditions and the pH value in the

373	solvent have a significant effect on the decomposition of amino acids (Abdelmoez et
374	al., 2007). The major N-containing components from the protein showed a small
375	difference in both the middle range condition and various moderate conditions
376	according to the previous study (Teri et al., 2014). It was also revealed that the main
377	composition of the solid products derived from the protein showed a little variation
378	within a certain range of reaction times and temperatures. Indeed, the total
379	N-containing compounds after the polymerisation for the solid product from the
380	protein were very similar.
381	4. Conclusions
382	In this paper, the morphology of the carbon-containing substances and the
383	microstructure of char derived from SS and its relevant model compounds have been
384	investigated. The G, D, and Kekule bands of SS and the char have been categorised
385	according to their locations and intensities. It was revealed that these bands are almost
386	the main aromatic vibrational bands in the whole sample. The results of the D/G ratio
387	indicate that six or more benzene rings were formed during the HTC process.
388	Furthermore, the dehydrogenation of the hydroaromatics and subsequent formation of
389	aromatic rings occur at 260 $^{\circ}$ C. It is believed that ZSM-5 with a high Si/Al ratio has a
390	positive effect on the graphite degree under a moderate hydrothermal temperature of
391	260 °C. Compared with the smaller Si/Al ratio of 38, the higher ratio favoured
392	depolymerisation of C-(C,H) during the HTC process. For the model compounds,
393	cellulose has a dramatic influence on the depolymerisation of C-(C,H). The char
394	derived from glucose, cellulose, and lignin has several similar carbon-containing

395	groups, such as COOR, R-C=O, and C-OR. The char surface morphology evolution
396	indicated that individual model compounds have different influences on the surface
397	morphological characteristics. Smaller particles were obtained with the ZSM-5
398	assistance during the SS treatment. Finally, three reaction pathways from SS and its
399	relevant model compounds to char have been proposed. This work provides insight
400	into the morphology and microstructure of catalytic HTC process from SS and its
401	model compounds, and may provide better understanding of the char structure and the
402	HTC process mechanism.
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Fig.1. Raman spectra deconvolution with fitting curve (G, G<sub>R</sub>, V<sub>L</sub>, V<sub>R</sub>, D, S<sub>L</sub>, S,
S<sub>R</sub>) of the bands in the 1000–1800 cm<sup>-1</sup> range for the SS and its relative model

- 574 compounds derived char (MC: Model compounds mixture, SP: Soybean protein,
- 575 L: Lignin, C: Cellulose, G: Glucose ).

## 576 Table 1 Summary of typical bands for Raman spectra(Tuinstra and Koenig, 1970;

577 **Zhao et al., 2016**)

Name		Position	Description
		(cm <sup>-1</sup> )	
G Band		1580	Graphite; aromatic ring; C=C
	G <sub>R</sub>	1540	Small Aromatics rings (3–5 rings)
Kekule	$V_L$	1465	C-H <sub>3</sub> or C-H <sub>2</sub> ; semi-circle breathing of aromatic
Band			rings;
	V <sub>R</sub>	1380	Methyl; aromatic rings; amorphous carbon;
D Band		1310	highly ordered carbonaceous materials; C-C
$S_L$ Band		1230	Aryl-alkyl ether; para-aromatics
S Band		1180-1100	aromatic ethers; C–C;
$S_R$ Band		1100-1050	C–H on arene rings; benzene ring



579 Fig.2. Comparison of band area ratios as a functional parameter among the



## 580 hydrothermal conversion chars derived from SS and its model compounds.



582 Fig.3. The XPS C 1s spectra for SS, its derived char, and char derived from its

583 model compounds





585 Fig.4. Percentage content of carbon-containing functional groups C-H, C-(C,H),

586 C-OR, C-(O,N), R-C=O, and COOR during HTC process.



Fig.5. SEM micrographs of (a) SS, char produced at 260 °C from (b) SS by hydrothermal process, (c) SS with ZSM-5 catalyst (Si/Al:38), (d) SS with ZSM-5 catalyst (Si/Al:300), (e) model compounds mixture, (f) SP, (g) Lignin, (h) Cellulose, and (i) Glucose.